

Ground state of a spin-crossover molecule calculated by diffusion Monte Carlo

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Spin-crossover molecules have recently emerged as a family of compounds potentially useful for implementing molecular spintronics devices. The calculations of the electronic properties of such molecules is a formidable theoretical challenge, as one has to describe the spin ground state of a transition metal as the ligand field changes. The problem is dominated by the interplay between strong electron correlation at the transition-metal site and charge delocalization over the ligands, and thus it fits into a class of problems where density functional theory may be inadequate. Furthermore, the crossover activity is extremely sensitive to environmental conditions, which are difficult to fully characterize. Here we discuss the phase transition of a prototypical spin-crossover molecule as obtained with diffusion Monte Carlo simulations. We demonstrate that the ground state changes depending on whether the molecule is in the gas or in the solid phase. As our calculation provides a solid benchmark for the theory, we then assess the performances of density functional theory. We find that the low-spin state is always overstabilized, not only by the (semi-)local functionals, but even by the most commonly used hybrids (such as B3LYP and PBE0). We then propose that reliable results can be obtained by using hybrid functionals containing about 50% of exact exchange.

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I. INTRODUCTION

In nature, there is a vast class of molecules whose magnetic moment can be altered by an external stimulus. Typical examples of such molecules are the spin-crossover (SC) complexes,^{1,2} which, in their most abundant form, contain a Fe^{2+} ion in octahedral coordination³ and exhibit a transition from the low-spin (LS) (singlet) ground state ($^1A_{1g}$ symmetry in group theory notation) to a high-spin (HS) (quintet) metastable state ($^5T_{2g}$). Other examples are the cobalt dioxolene molecules.^{4–6} These undergo the so-called valence tautomeric interconversion (VTI), namely, an interconversion between two redox isomers, which differ in charge distribution and spin configuration. Both the SC transition and the VTI are usually observed for molecules in a single crystal and can be triggered by variations in temperature and pressure or by optical irradiation.⁷ Furthermore, it was also recently suggested that the VTI⁸ and the spin ground state of a two-center polar molecule⁹ can be controlled by a static electric field.

SC complexes are promising materials as candidates for molecular spintronics applications.^{10,11} Devices incorporating such molecules are predicted to display drastic changes in the current-voltage curve across the phase transition,^{12,13} and several transport experiments have recently achieved encouraging results. Alam *et al.*¹⁴ were able to distinguish the spin state of a SC molecule placed on graphite by scanning tunnel microscopy, while Prins *et al.*¹⁵ demonstrated that the temperature-dependent conductance of a device incorporating a SC cluster correlates well with the phase transition. In other cases, however, the data are not easy to interpret¹⁶ and the experimental investigations are combined with density functional theory (DFT) simulations. In principle, DFT should allow the computation of quantities not easily accessible by experiments and should also provide parameters for effective transport models. However, unfortunately, DFT results for SC

molecules depend strongly (even qualitatively) on the choice of the exchange-correlation functional used^{17–22} and no standard has yet emerged. In other words, DFT is still not a predictive theory for the problem.

This is indeed a major issue, since higher-level theories such as wave-function-based quantum chemistry methods are too computationally demanding for tackling the problem of SC molecules on surfaces. One should then benchmark DFT for a problem simple enough to be addressable by both DFT and wave-function methods and use this to establish which are the most appropriate DFT exchange and correlation functionals to use. This task, however, is complex, as a direct comparison with experiments is often impossible, since the experimental conditions (solid-state phase stabilized by counter ions) are different from those accessible by the computational setup (a single molecule in vacuum).^{18,19,22,23} In this work, we address in detail such an issue and establish a solid theoretical benchmark for the theory for a molecule for which experimental results are available. In particular, we perform diffusion Monte Carlo (DMC)²⁴ calculations for the molecule $[\text{FeL}_2](\text{BF}_4)_2$ ($\text{L} = 2,6\text{-dypirazol-1-yl-4-hydroxymethylpyridine}$) at both the DFT-relaxed and the experimental coordinates.

We find that the molecule in the gas phase presents a high-spin ground state, i.e., it cannot undergo any spin-crossover transition. However, the robustness of the high-spin state is weakened when one considers the atomic coordinates for the molecule in the crystal phase (as obtained by x-ray data), and eventually the ground state becomes low spin when dipolar contributions are also taken into account. This means that a spin-crossover molecule may not show any crossover activity at the single-molecule level, but that this can be achieved in a solid crystal. We then compare our results with those obtained by DFT. Intriguingly, local functionals predict the molecule in a low-spin ground state even in the gas phase, in contrast to the DMC results. In contrast, hybrids functionals correct this

shortcoming and provide a reliable description of the ground state.

The paper is organized as follows. In the next section, we provide a detailed description of the problem at hand and discuss its major difficulties. Then we briefly describe the computational methods used, before moving to the presentation of our results. Finally we conclude.

II. PROBLEM STATEMENT

Predicting the ground state of a magnetic molecular object is not a straightforward task. High-level quantum-mechanical calculations based on wave-function methods are too computationally demanding to be used routinely and DFT is not reliable enough, as the results often depend sensibly on the approximation taken for the exchange and correlation functional. Most of the local and semilocal DFT functionals underestimate the exchange energy and, consequently, they tend to favor the LS state of a magnetic ion over the HS one.^{17,22} In spin-crossover molecules, this shortcoming often leads to such large errors that even stable HS molecules are described as LS.^{18,19} In contrast, the most commonly used hybrid functionals are believed to overstabilize the HS state,^{25,26} so that it remains unclear what is the best functional to use. The solution is often to perform calculations with different functionals and then compare the results against available experimental data.

However, several authors^{18,19,22,23} have criticized this common practice of assessing the performances of the various functionals against experiments. In fact, on the one hand, many experiments that addressed how the SC transition is affected by the counter ions, the solvent and the strain of the ligands, demonstrated that the properties of SC complexes depend drastically on environmental conditions.^{27–29} On the other hand, DFT calculations usually refer to molecules in the gas phase, and consider only the cationic unit and neglect completely those effects. Therefore, one can wonder whether the ground state of the molecule in the condensed phase is the same as that of the molecule in the gas phase and whether the DFT results can really be compared to the available experimental data. Thus, the questions become (1) is the spin ground state of the cationic unit the same as that of the full molecule in crystals, and (2) can we produce a robust benchmark for DFT against the problem of predicting the physics of SC compounds? As no experiment has ever been performed, to our knowledge, for SC molecules in the gas phase, *ab initio* methods more accurate than DFT have to be considered in order to answer these questions.

In the past, wave-function-based methods have been used for this problem.^{16,18–21} However, as the authors themselves pointed out, the results were plagued by systematic errors ascribed to the limited basis set used for Fe^{2+} and by the fact that the methods themselves neglect dynamic correlation (although this can be partly accounted for through a perturbative treatment). Here we propose an alternative route and perform diffusion Monte Carlo (DMC)²⁴ calculations for a prototypical Fe^{2+} spin-crossover molecule. Unfortunately, the small number of applications of DMC to transition-metal complexes has not yet demonstrated how accurate DMC is for these systems.³⁰ However, as electron correlation is treated

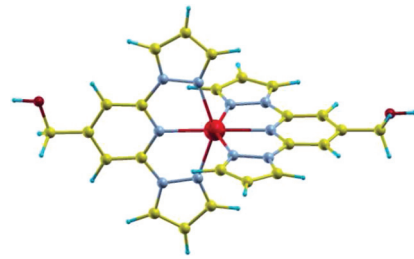


FIG. 1. (Color online) The cationic unit $[\text{FeL}_2]^{2+}$ ($\text{L} = 2,6\text{-dypirazol-1-yl-4-hydroxymethylpyridine}$) used in the DMC calculations. Color code: C: yellow; O: red (small sphere); Fe: red (large sphere); N: gray; H: blue.

in a proper many-body fashion, DMC is expected to outperform DFT and our calculation provides a solid benchmark for assessing the performances of DFT. In particular, we consider the molecule $[\text{FeL}_2](\text{BF}_4)_2$ ($\text{L} = 2,6\text{-dypirazol-1-yl-4-hydroxymethylpyridine}$)³¹ (see Fig. 1). We show that the ground state of the cationic unit (which we will generally refer to as the molecule) in the gas phase is HS, but that a phase transition may exist in the solid state due to a number of crystal-related effects.

We then show that the same result can be obtained by DFT hybrid functionals containing approximately 50% of exact exchange, thus confirming early calculations for model molecules.²³ This establishes a recipe for the use of DFT for this class of materials and it opens the opportunity to investigate with confidence the spin-crossover transition of molecules in different environments (for instance, on surfaces).

III. COMPUTATIONAL DETAILS

DFT calculations are performed with the NWCHEM code.³² We use several functionals belonging to different classes: (1) the Vosko-Wilk-Nussair local-density approximation (LDA),³⁴ (2) the generalized gradient approximation (GGA) referred as BP86, which combines the Becke88 exchange functional³⁵ with the Perdew86 correlation one,³⁶ and (3) the hybrid functionals B3LYP,³⁷ PBE0,^{38,39} and the Becke-HH,⁴⁰ which include, respectively, 20%, 25%, and 50% of exact exchange. We also consider a reparametrization of the B3LYP functional, called B3LYP*, which includes only 15% of HF exchange. This was introduced by Reiher and co-workers specifically in order to describe Fe^{2+} complexes.^{25,26} The Ahlrichs triple- ζ polarized basis set³³ is used throughout.

DMC calculations are performed using the CASINO code.⁴¹ The trial wave function has a Jastrow-Slater form.²⁴ The imaginary-time evolution of the Schrödinger equation has been performed with the usual short-time approximation, and time steps of 0.0125 and 0.005 a.u. are used. Dirac-Fock pseudopotentials^{42,43} with the “potential localization approximation”⁴⁴ have been used. The single-particle orbitals of the trial wave function are obtained through (LDA) DFT calculations performed with the plane-wave code QUANTUM ESPRESSO.⁴⁵ The same pseudopotentials used for the DMC calculations are employed. The plane-wave cutoff is fixed at 300 Ry and the plane waves are reexpanded in terms of B splines.⁴⁶ The B -spline grid spacing is $a = \pi/G_{\text{max}}$, where G_{max} is the length of the largest vector employed in the

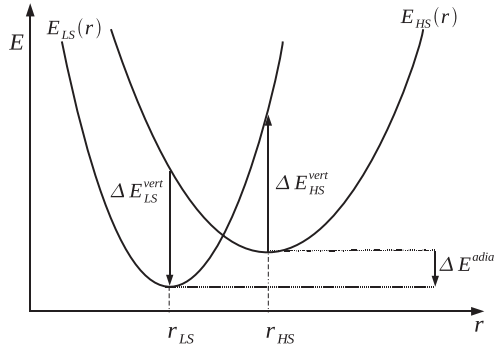


FIG. 2. Potential-energy surface of the HS and LS state of a SC molecule. The collective coordinate r represents all of the nuclear coordinates of the molecule and interpolates between the LS and the HS geometries. The adiabatic energy gap ΔE^{adia} and the vertical energy gaps $\Delta E_{\text{LS}}^{\text{vert}} = \Delta E^{\text{vert}}(r_{\text{LS}})$ and $\Delta E_{\text{HS}}^{\text{vert}} = \Delta E^{\text{vert}}(r_{\text{HS}})$ are also indicated.

calculations. Periodic boundary conditions are employed for the plane-wave DFT calculations and supercells as large as 40 Å are considered. In contrast, no periodic boundary conditions are imposed with DMC.

IV. RESULTS AND DISCUSSION

The crucial quantity for understanding the spin-crossover transition is the potential-energy surface, schematically displayed in Fig. 2. This is typically plotted for the two different spin configurations as a function of a collective reaction coordinate r , which interpolates the molecule geometry along the LS-to-HS phase transition. In our case, DMC and DFT are used to compute the “adiabatic energy gap”²² defined as

$$\Delta E^{\text{adia}} = E_{\text{HS}}(r_{\text{HS}}) - E_{\text{LS}}(r_{\text{LS}}), \quad (1)$$

where r_{LS} (r_{HS}) and $E_{\text{LS}}(r_{\text{LS}})$ [$E_{\text{HS}}(r_{\text{HS}})$] represent, respectively, the geometry and the total energy of the LS-singlet (HS-quintet) state. When studying SC molecules at zero temperature, ΔE^{adia} is the central quantity, as it indicates whether the molecule ground state is LS ($\Delta E^{\text{adia}} > 0$) or HS ($\Delta E^{\text{adia}} < 0$). We also calculate the “vertical energy gaps”²²

$$\Delta E^{\text{vert}}(r_{\text{LS}}) = E_{\text{HS}}(r_{\text{LS}}) - E_{\text{LS}}(r_{\text{LS}}), \quad (2)$$

$$\Delta E^{\text{vert}}(r_{\text{HS}}) = E_{\text{HS}}(r_{\text{HS}}) - E_{\text{LS}}(r_{\text{HS}}), \quad (3)$$

where $E_{\text{HS}}(r_{\text{LS}})$ [$E_{\text{LS}}(r_{\text{HS}})$] is the energy of the quintet (singlet) state for the r_{LS} (r_{HS}) geometry (see Fig. 2).

DMC calculations were first carried out by using the molecular geometries optimized with DFT for the molecule in the gas phase. The Fe-ligand bond lengths computed with the various functionals are listed in Table I. As the DMC energy differences between the geometries calculated from the various exchange and correlation functionals are of the same order of magnitude as the Monte Carlo statistical error, we have not been able to firmly establish which functional produces the best structure. We have, therefore, decided to present results only for the structures relaxed with B3LYP, keeping in mind that they are essentially valid also for the structures obtained with the other functionals.

TABLE I. Experimental and calculated Fe-N bond lengths for the $[\text{FeL}_2]^{2+}$ cation. The number of bonds of a given length is indicated inside the bracket. The average difference between HS and LS Fe-N bond lengths is about 0.2 Å, which is a typical value for SC molecules.

Spin state		d (Å)
GGA (BP86)	LS	1.898(2), 1.958(4)
GGA (BP86)	HS	2.118, 2.127, 2.159, 2.166, 2.185(2)
B3LYP*	LS	1.923(2), 1.996(4)
B3LYP*	HS	2.182(2), 2.211(2), 2.207(2)
B3LYP	LS	1.933(2), 2.011(4)
B3LYP	HS	2.185(2), 2.218(2), 2.222(2)
PBE0	LS	1.910(2), 1.984(4)
PBE0	HS	2.169(2), 2.1965(4)
Expt.	LS	1.909, 1.991, 1.912, 1.985, 1.980, 1.992
Expt.	HS	2.105, 2.163, 2.103, 2.160, 2.170, 2.153

The DMC adiabatic energy gap is reported in Table II. Our result indicates that the molecule in the gas phase is in its high-spin state, in contrast to the common belief and to the experimental result for the single crystal. Such a ground state is indeed quite robust, as DMC gives us an adiabatic energy gap of -1.20 eV. Since DMC provides an unequivocal assignment of the molecule ground state, it essentially establishes that no spin-crossover transition is expected for $[\text{FeL}_2]^{2+}$ in the gas phase. Hence, in order to account for the experimentally observed SC transition, one needs to understand how the embedding of the molecule in a crystal is able to reverse the relative order of the HS and LS states at zero temperature, i.e., to change the sign of ΔE^{adia} .

Here we cannot avail of DMC calculations directly because the supercell needed to describe the single crystal, including counter ions, is too big to be handled by DMC. As such, we just provide an estimate and our argument proceeds as follows. First, one has to repeat the calculations using the experimental geometries measured for the molecule in the crystal form.³¹ These are less symmetric and present shorter metal-ligand bond lengths than those optimized in the vacuum (see Table I). The result is that the DMC-calculated ΔE^{adia} gets smaller, although it maintains the negative sign (compare Table II with Table III). Second, the electrostatic potential felt by the molecule in the crystal and due to both the counter ions and the other molecules needs to be taken into account.

Since the molecule in the different spin states presents a different electrical dipole, it is expected that such a mean-field

TABLE II. Adiabatic and vertical energy gaps for the $[\text{FeL}_2]^{2+}$ cation calculated with DFT and DMC at the DFT-B3LYP relaxed geometry. The relative Monte Carlo statistical error is indicated in brackets.

Method	$\Delta E^{\text{vert}}(r_{\text{LS}})$ (eV)	$\Delta E^{\text{vert}}(r_{\text{HS}})$ (eV)	ΔE^{adia} (eV)
GGA (BP86)	2.87	-0.180	1.23
B3LYP*	1.97	-1.013	0.331
B3LYP	1.54	-1.23	0.012
PBE0	1.19	-1.74	-0.23
Becke -HH	0.51	-2.50	-1.33
DMC ($\Delta\tau = 0.005$ a.u.)	0.28(4)	-2.57(4)	-1.19(4)

TABLE III. Adiabatic and vertical energy gaps for the $[\text{FeL}_2]^{2+}$ cation calculated with DMC at the single-crystal experimental geometry. We report DMC results for two values of the imaginary time. The relative Monte Carlo statistical error is indicated in brackets. The experimental molecular structure used for the calculation is taken from the x-ray data of Ref. 31.

	$\Delta E^{\text{vert}}(r_{\text{LS}})$ (eV)	$\Delta E^{\text{vert}}(r_{\text{HS}})$ (eV)	ΔE^{adia} (eV)
DMC ($\Delta\tau = 0.0125$ a.u.)	0.65(3)	-1.90(2)	-0.36(4)
DMC ($\Delta\tau = 0.005$ a.u.)	0.65(3)	-1.91(3)	-0.36(4)

electrostatic potential produces a relative shift of the HS and LS potential-energy surfaces. The magnitude of this shift, which tends to stabilize the LS state, has been recently estimated^{47,48} to be about 0.5 eV. Note that this is simply an estimate obtained by summing up classical electrical dipoles. Unfortunately, the relative shift of the HS and LS potential-energy surfaces depends on the nature of the counter ions and an exact estimate will require a calculation for the unit cell of the molecular crystal. Such a calculation is, however, too computationally expensive to be performed. Therefore, here we just follow the estimate of Refs. 47 and 48, and we provide only a figure of merit for such shift. When the effect of the geometry and the electrostatic corrections are both included, DMC allows us to estimate a ΔE^{adia} for the condensed phase of about 0.2 eV. This is now positive, i.e., the ground state is LS and is very close to the typical values of the adiabatic energy gap inferred from experimental data.⁴⁹

We finally turn our attention to the assessment of the performances of the various exchange-correlation functionals. Table II displays the vertical and adiabatic energy gaps calculated with DFT. We note that our GGA functional (BP86) underestimates the exchange so significantly that the molecule is predicted to be stable in the LS state ($\Delta E^{\text{adia}} > 0$). Furthermore, the absolute value of $\Delta E^{\text{vert}}(r_{\text{LS}})$ [$\Delta E^{\text{vert}}(r_{\text{HS}})$] is much larger than the corresponding one computed with DMC. This means that standard GGAs, such as BP86, predict a very stable low-spin ground state. B3LYP and PBE0 improve only slightly the accuracy of the calculated gaps and the LS state still remains massively overstabilized. In contrast, as in the case of small Fe^{2+} model complexes,²³ HH is found to be the functional that performs better, yielding a fair agreement with the DMC gaps.

Importantly, our analysis demonstrates that the assessment of the performances of a given DFT functional can be completely erroneous if one insists on comparing the total energies calculated for the gas phase directly to experiments. If this was done with our DFT data, we would have concluded, as other authors did,^{25,26} that B3LYP* was the best functional. Our analysis instead demonstrates that the correct assignment needs to be done against a reliable benchmark, with the result that the best-suited functional must carry a fraction of exact exchange close to 50%.

V. CONCLUSION

In conclusion, we have performed accurate DMC calculations investigating the ground state of the molecule $[\text{FeL}_2]$ (BF_4)₂ ($\text{L} = 2,6\text{-dypirazol-1-yl-4-hydroxymethylpyridine}$), an experimentally well-characterized prototype belonging to the SC Fe(II) family. We have found that in the gas phase, the ground state is high spin, so that no spin-crossover transition is predicted. However, if one performs the calculations at the experimental atomic coordinates, then the adiabatic gap between the low-spin and high-spin solution reduces dramatically and eventually turns in favor of the low-spin state as dipolar corrections are included. These mimic the electrostatic interaction in a crystal and establish that the molecule is indeed low spin, but only when it is part of a crystal in a condensed solid-state phase.

Our DMC results then establish a rigorous benchmark for more approximated theories such as DFT. In this spirit, we have performed calculations by exploring different approximations of the exchange and correlation functional. We have demonstrated that a hybrid functional, including 50% of exact exchange (HH), is able to provide a quite accurate estimate of the energetic of the molecule, i.e., it matches closely the DMC results. This contains a significantly larger fraction of Hartree-Fock exchange than what was previously believed. As such, our results have a twofold importance. On the one hand, they shed light on the longstanding issue of establishing the ground state of SC complexes. On the other hand, they provide a recipe of how to perform such types of calculations for real molecules not addressable by wave-function-based methods.

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